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# Photocatalytic reaction kinetics model based on electrical double layer theory
## Ⅱ. Infrared spectroscopic characterization of methyl orange adsorption on $TiO_2$ surface①

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**[Abstract]** In the process of heterogeneous photo-catalytic degradation, the reaction rate depends strongly on the property of organic binding on the surface. It is important to identify the adsorption of organic compounds on $TiO_2$ surface to understand the mechanism of degradation and proper kinetics expression. The infrared spectroscopy was used to analyze the methyl orange adsorption on $TiO_2$ surface in aqueous solutions in different pH ranges. The variation of the surface complexation of methyl orange formed on the $TiO_2$ surface in different acid and basic media was discussed. And the adsorption amounts were also qualitatively analyzed. Methyl orange has strong, weak and little adsorption on the $TiO_2$ surface in acid, basic and near neutral solution, respectively.

**[Key words]** infrared spectroscopy; adsorption; methyl orange; $TiO_2$
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## 1 INTRODUCTION

Heterogeneous photo-catalysis shows great potential for applications in gaseous or aqueous organic contaminants decontamination. However, its low photo-catalytic reaction rate limits its practical applications. This has lead to considerable interest in examining the mechanistic details of the $TiO_2$ photo-reactivity in an effort to improve its photo-catalytic activity[1~6].

There are some effective ways to promote the photo-catalytic activity, including the extension of optical absorption, more efficient separation of electron/hole pairs and more efficient adsorption on photo-catalysts surfaces. Numerous reports[4, 5] focus on seeking for ways to extend the optical absorption to visible range and to promote the separation of electron/hole pairs. However, few literatures dealt with the adsorption-desorption process of organic matter on $TiO_2$ surface. In fact, photo-catalytic oxidation reaction takes place on the surface of $TiO_2$ but not in the bulk solution. Most experimental reports[6] relating to the kinetics of photo-catalysis were expressed by using Langmiur-Heinshelwood adsorption equation or psuedo-first kinetic model. The further study on the relationship between adsorption and photo-catalytic reaction rate was rarely reported. And at the interface between organic compounds and $TiO_2$, the nature of the adsorbate-oxide binding is poorly understood. It is necessary to study the adsorption process of organic matter on the surface of $TiO_2$ in order to disclose the photo-catalytic degradation mechanisms of organic moleculae.

In the process of heterogeneous photo-catalytic degradation, the reaction rate depends strongly on the property of the organic binding on the surface[7]. The surface complexation formed in the inner layer (chemical-adsorption) can directly accomplish electron transfer process between the hole and organic moleculae. And that formed in the outer layer (physico-adsorption) can only be oxidized by hydroxide radical generated from the hole. Different adsorption mechanisms of organic compounds on $TiO_2$ surface can cause different reaction rates and byproducts. It is important to identify the adsorption of organic matter on $TiO_2$ surface for understanding the mechanism of degradation and proper kinetics expression. Infrared spectrum is an effective characterization method to disclose the adsorption mechanism of organic compounds. In the paper, the adsorption of methyl orange on the surface of $TiO_2$ in different pH solutions was characterized by infrared spectrum, and the adsorption

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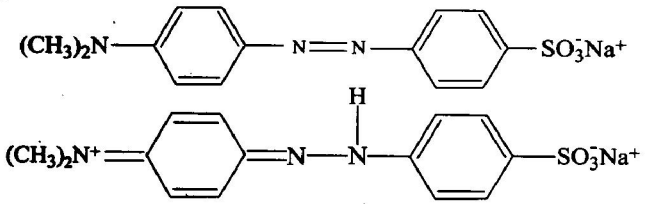
mechanism was proposed.

## 2 EXPERIMENTAL

All the reagents used in this paper were on analytical grade and used without further purification. $TiO_2$ was purchased from Japan Titan Kogyokk Co. The BET surface area was 61 $m^2/g$. Based on the X-ray diffraction measurement, no other crystal besides anatase could be detected.

Methyl orange has been chosen as an objective organic matter with different molecular formulae, including quinone and azo structures( as shown below ) in different pH solutions with different colors.




$TiO_2$, weighed by analytical balances, was added into the beaker containing methyl orange solution with 200 mL volume. Then KOH was added and stirred for half an hour. The experimental procedure was described as follows: putting 20 mL suspension into the beakers, respectively; adding HCl to adjust pH; stirring for 24 h in dark. The powder samples were obtained by filtration of suspension and dried under infrared light, and named as methyl orange/$TiO_2$. Methyl orange/$TiO_2$ samples were briquetted after mixed with KBr. Then FTIR spectra were recorded by FT-740 model infrared spectra instrument.

## 3 RESULTS AND DISCUSSION

### 3.1 Infrared spectrum of $TiO_2$ powder

The infrared spectrum of $TiO_2$ is shown in Fig. 1. $TiO_2$ powder has strong infrared absorption at 542. 54 $cm^{-1}$ and another absorption at 3419. 51 $cm^{-1}$, which are the bending and flex oscillations of hydroxide on $TiO_2$ surfacerespectively. There is no absorption in the range of 3000 ~ 900 $cm^{-1}$ besides a weak absorption peak at 1 600 $cm^{-1}$. So the organic surface complexation can be well characterized in the range. The peak at 542. 54 $cm^{-1}$ is the characteristic absorption peak of $TiO_2$.

### 3.2 Infrared spectra of methyl orange/ $TiO_2$

The infrared spectra of methyl orange adsorbed on the surface of $TiO_2$ varied with pH value and its concentration in the solution. When the concentration of methyl

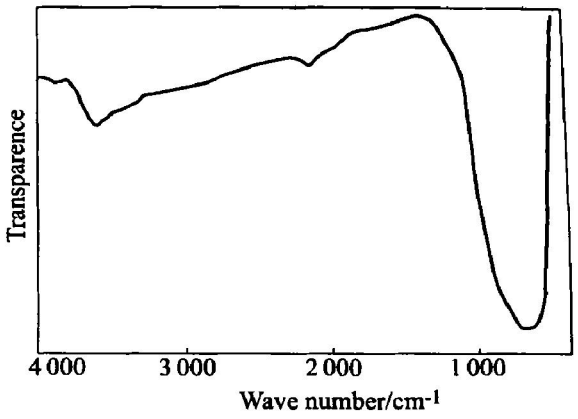



**Fig. 1** Infrared spectroscopy of $TiO_2$ powder

orange is 20 $mg \cdot L^{-1}$, the infrared spectra of the methyl orange/$TiO_2$ at different pH values are shown in Fig. 2 and their magnified spectra at pH= 2. 57 and pH= 9. 18 are shown in Fig. 3. Compared with the infrared spectrum of $TiO_2$ powder, it is shown that methyl orange/$TiO_2$ had strong, a little and little adsorption in acid, basic and near neutral solution, respectively in the range of 3 000~ 900 $cm^{-1}$. In acid solution, the spectra were dominated with a strong band at 1 400 $cm^{-1}$, which indicates that the $-N=N^+-$ group exist in methyl orange/$TiO_2$ surface complexation. In basic solution, the adsorption band near 1 123. 4 $cm^{-1}$ is the characteristic absorption peak of sulfonic group[8].

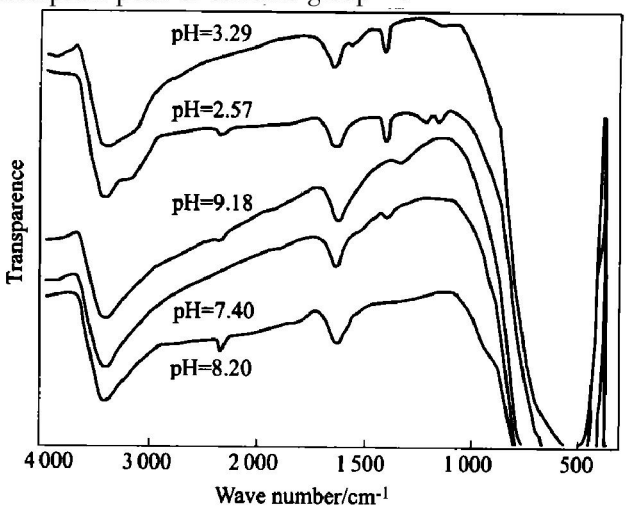



**Fig. 2** Infrared spectra of methyl orange/$TiO_2$ varying with different pH values at concentration of 20 $mg \cdot L^{-1}$

The infrared spectra of methyl orange/$TiO_2$ have some more obvious peaks with higher methyl orange concentration. When the concentration of methyl orange is 60 $mg \cdot L^{-1}$, the infrared spectra of the methyl orange/$TiO_2$ at pH= 2. 57 and pH= 9. 18 are shown in Fig. 4 and their magnified spectra are shown in Fig. 5. The adsorption band at 1 384 $cm^{-1}$, which indicates the presence of $-^+C=N-$ group in the methyl orange/

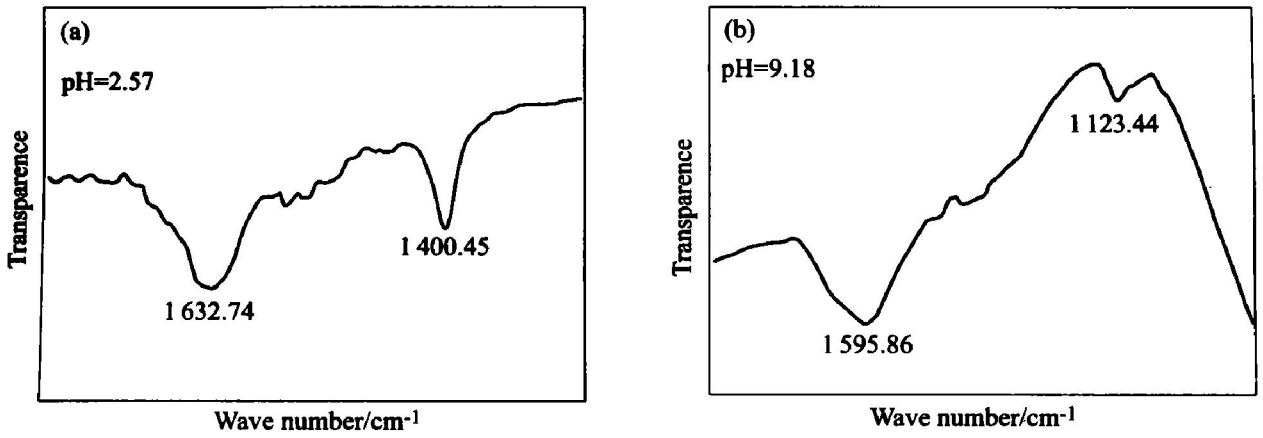



**Fig. 3** Magnified infrared spectra in Fig. 2 at pH= 2. 57(a) and pH= 9. 18(b)

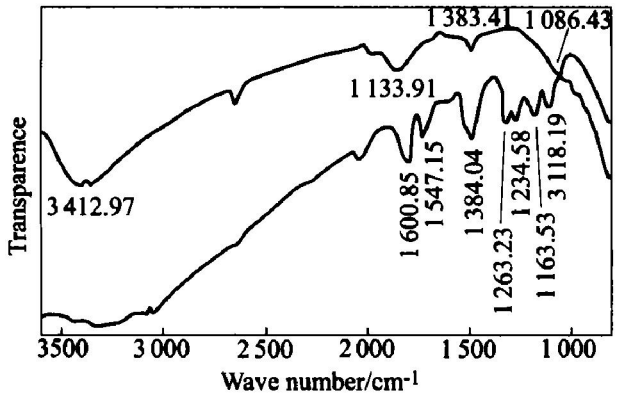



**Fig. 4** Infrared spectra of methyl orange/$TiO_2$ with concentration of 60 mg·$L^{-1}$ at pH= 2. 11(bottom) and pH= 10. 53(top)

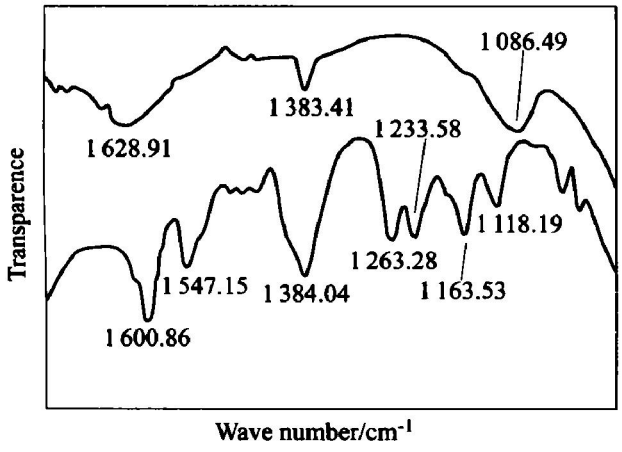
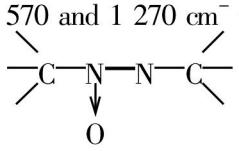



**Fig. 5** Magnified infrared spectra in Fig. 5 at pH= 2. 11(bottom) and pH= 10. 53(top)

$TiO_2$ surface complexation, appears obviously in both acid and basic solutions. The spectrum in acid solution is more obvious than that in basic solution. The adsorption bands near 1 600 $cm^{-1}$ and 1 547 $cm^{-1}$ are attributed to double bond flexing oscillation in different conjugate systems. The absorption bands near 1 163 $cm^{-1}$ and 1 028 $cm^{-1}$ are the characteristic absorption peaks of sulfonic acid. Compared to the infrared spectrum of methyl orange (as shown in Fig. 6), two new conjugate absorption bands appear near 1 263 $cm^{-1}$ and 1 233 $cm^{-1}$, which indicate that methyl orange is chemr adsorbed on the surface of $TiO_2$. The peaks at 1 263 $cm^{-1}$ and 1 233 $cm^{-1}$ might be attributed to the flexing oscillation of O ←N bond. Oxyazo compound with the absorption bands of —N ═ N — and N → O might appear at 1 570 and 1 270 $cm^{-1}$ respectively in the structure of  . The absorption bands near 3 415 $cm^{-1}$, 3 472 $cm^{-1}$, 2 901 $cm^{-1}$ were the characteristic adsorption of hydroxyl on the surface of $TiO_2$, aminogroup and methylene in methyl orange molecule.

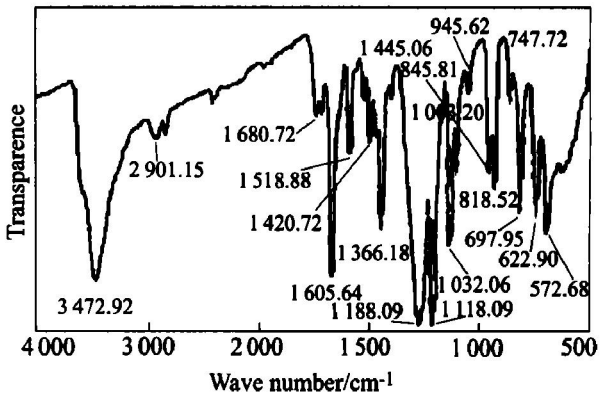



**Fig. 6** Infrared spectrum of methyl orange

### 3.3 Adsorption models at different pH values

The strong dependence of the capacity of $TiO_2$ towards methyl orange adsorption under different pH values might be explained by taking into account the intrinsic amphoteric behavior of suspended $TiO_2$ particles and the acidic-basic nature of the organic. It is well known that metal oxide particles suspended in solution behave similarly to diprotic acids. As for $TiO_2$, hydroxyl groups undergo the following acid-base equilibria:[9]

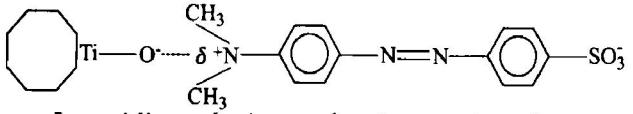
$$\equiv TiOH_2^+ \overset{pK_{a1}}{\rightleftharpoons} \equiv TiOH + H^+ \quad (1)$$

$$\equiv TiOH \overset{pK_{a2}}{\rightleftharpoons} \equiv TiO^- + H^+ \quad (2)$$

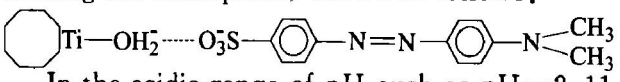
where $\equiv$TiOH represents the 'titanol' surface group and $pK_{a1}$, $pK_{a2}$ are the negative logs of the acidity constants for the first (Eqn. (1)) and second (Eqn. (2)) acid dissociation, respectively. As for the $TiO_2$, the zero point of charge equals 6.58[10]. From the above analyses, it is reasonable to expect that adsorption on $TiO_2$ surface will depend strongly on the electrical charge of the organic moleculae and the photocatalyst surface.

Methyl orange has a negatively charged sulfonic group and it is expected that, at low pH, attractive forces between the $TiO_2$ surface and the methyl orange will favor adsorption. On the other hand, when pH value is higher than 6.58, the $TiO_2$ surface is negatively charged and repulsive forces will lead to the decrease of adsorption. Finally, at pH values close to the pHzpc, the adsorption is expected to take intermediate values. The dependence of the adsorption capacity of $TiO_2$ towards methyl orange on the pH of the solution (Fig. 3) experimentally observed was not well in agreement with the explanation given above, because the adsorption is affected by the properties of organic moleculae besides the pH value of the solution affecting the electrical properties of the $TiO_2$ surface.

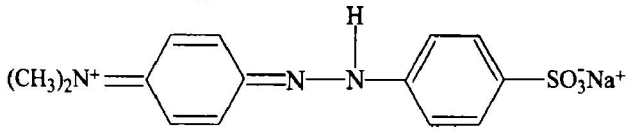
Since the amino group of the methyl orange molecule also has a partial positive charge[11] with respect to benzene ring, this group may also bind with the $TiO^-$ of the $TiO_2$ surface in basic solution, which may increase the adsorption. The methyl orange/$TiO_2$ surface complexation in basic pH solution could be shown as follows:



In acidic solution, the interaction between protonated titanol and the negatively charged sulfonic group of methyl orange, is one of the factors affecting the adsorption, shown as follows:

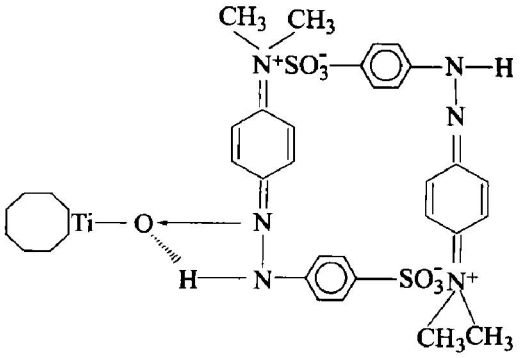


In the acidic range of pH such as pH = 2.11, the methyl orange will exist in azo structure,



—N = N—

In the molecule of azo structure may establish O ← N bond with titanol on $TiO_2$ surface, resulting in the chemr-adsorption of methyl orange on the $TiO_2$ surface. And the adsorbed azo structure molecule can adsorb another layer methyl orange moleculae by the electrostatic interaction as shown as follows:



## [REFERENCES]


[1] LI Xin-Jun, LI Fang-Bai, GU Guo-bang, et al. The preparation of nanometer-sized magnetic photocatalysts and their photocatalytic activity and properties[J]. The Chinese Journal of Nonferrous Metals, 2001, 11(6): 971-976.

[2] Choi W, Termin A, Hoffmann M R. The role of metal ion dopants in quantum-sized $TiO_2$: correlation between photoreactivity and charge carrier recombination dynamics[J]. J Phys Chem, 1994, 98: 13669-13679.

[3] LI Fang-bai, GU Guo-bang, LI Xin-Jun, et al. The enhanced photocatalytic behavior of $Sb_2O_3/TiO_2$ semiconductor nanopowder[J]. Chinese Journal of Inorganic Chemistry, 2001, 17: 37-42.

[4] Li X Z, Li F B. Study of Au/$Au^{3+}$-$TiO_2$ Photocatalysts toward visible photooxidation for water and wastewater treatment[J]. Environ Sci & Technol, 2001, 35: 2381-2387.

[5] LI Fang-bai, GU Guo-bang, LI Xin-Jun, et al. The preparation, characterization and its photocatalytic behavior of $WO_3/TiO_2$ coupled semiconductor nanopowder[J]. Acta Physico-Chimica Sinica, 2000, 16: 997-1001.

[6] Xu Yi-ming, Langford Cooper H. Variation of Langmuir adsorption constant determined for $TiO_2$-photocatalyzed degradation of acetophenone under different light intensity[J]. Journal of Photochemistry and Photobiology A: Chemistry, 2000(133): 67-71.

[7] Minero C. Kinetic analysis of photoinduced reactions at the water semiconductor interface[J]. Catalysis Today, 1999 (54): 205-216.

[8] Bellamy L J. The Infrared Spectra of Complex Molecules [M]. New York: John Wiley, 1958.

[9] Kiriakidou F, Kondarides D I, Verykios X E. The effect of operational parameters and $TiO_2$-doping on the photocatalytic degradation of azo-dyes[J]. Catalysis Today, 1999 (54): 119-130.

[10] LI Xin-jun, LI Fang-bai, HE Ming-Xing, et al. A photocatalytic reaction kinetics model based on electrical double layer theory, I. The surface complexation model at the $TiO_2$/Water interface[J]. Trans Nonferrous Met Soc China, 2002, 12(4): 792-797.

[11] Robert D, Weber J V. Photocatalytic degradation of methylbutandioic acid (MBA) in aqueous $TiO_2$ aqueous: influences of MBA adsorption on the solid semi-conductor [J]. J Cleaner Production, 1998, 6: 335-338.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